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ANNOUNCEMENT.

This paper on a "New Method for Determining Compressibility" has been prepared by Professor Theodore W. Richards, Ph.D., Professor of Chemistry in Harvard University, and his assistant, Wilfred N. Stull, S.M. (Iowa University), Edward Austin Fellow of Harvard University. Its publication by the Carnegie Institution is recommended by these chemists: Professors Ira Remsen, of the Johns Hopkins University; F. W. Clarke, of the United States Geological Survey, and Edgar F. Smith, of the John Harrison Laboratory in the University of Pennsylvania.

This investigation was made in the Chemical Laboratory of Harvard College, Cambridge, Massachusetts, and the expense of it was defrayed, in the earlier part, by the Cyrus M. Warren fund of Harvard University, and in the latter part, by the Carnegie Institution of Washington.

DANIEL C. GILMAN,
President of the Carnegie Institution.

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NEW METHOD FOR DETERMINING COMPRESSIBILITY,

WITH APPLICATION TO BROMINE, IODINE, CHLOROFORM, BROMOFORM, CARBON TETRACHLORIDE, PHOSPHORUS AND WATER.

BY THEODORE WILLIAM RICHARDS AND WILFRED NEWSOME STULL.

INTRODUCTION.

IT has been suggested recently that since the volume of a solid or liquid must be determined in part by the internal pressures to which it is subjected by chemical affinity and cohesion, the compressibilities of substances are probably data of important chemical significance.[1]

In attempting to interpret this significance, the enquirer at once faces the fact that few pertinent compressibilities are accurately known. Only complex organic compounds have been much studied, and their behavior under pressure is affected by too many variables to be easily interpreted. No more than four elements have been studied at all, and none except mercury and copper have been investigated by more than a single investigator.

In order to fill this important gap in physicochemical knowledge, the following investigation was undertaken. Its publication will be followed promptly by similar more extended publications, in which the compressibilities of as many elements and simple compounds as possible will be treated.

The determination of compressibility is sometimes considered as one of the most difficult of physical processes. The difficulty is due chiefly to the fact that under pressure all the parts of any apparatus change in volume, and hence the contraction under pressure of the substance under examination is partly hidden. Perhaps it is this difficulty, added to a lack of realization of the significance of the data, which has deterred investigators from undertaking the problem more systematically.

Among the various methods which have been used, those involving theoretical considerations of a mathematical nature, such as those computed from the coefficient of Poisson, are of somewhat doubtful value.

[1] Richards, Proc. Am. Acad. 37, 1 (1901), 399 (1902); 38, 293 (1902). Also Zeitschr. Phys. Chem. 40: 169, 597; 42: 129 (1902).

The combination of stresses involved is not simple enough for certain interpretation.

The method which attempts to correct itself by measuring the external change in volume of a bulb subjected to internal pressure is obviously faulty, as Amagat[1] has pointed out, because the erroneous assumption is made that the interior volume changes no more than does the exterior volume. Moreover, such an apparatus can endure but a small pressure, and it is difficult to enclose it in any other apparatus capable of withstanding pressure without hiding the substance under examination. Again, it is always possible that this substance may dissolve some of the fluid used to transmit the pressure, or be dissolved by it.

When a capillary glass tube is used to contain a liquid under examination, three serious errors are introduced. First, the bore and hence the volume of the tube increases under pressure. Next, the non-conducting nature of the walls prevents the compression from being strictly isothermal, while the heat capacity of the walls prevents it from being strictly adiabatic. From the work of Barus,[2] who has carried out the most successful and comprehensive experiments according to this method, it may be inferred that these errors in some cases nearly counterbalance one another. Another cause of error is the adhesion of the compressed liquid to the emptied tube, as the column shortens under pressure, a circumstance which causes the compression to appear too large. Moreover, the compressibility of liquids is so slight that very small changes in length of column must be accurately observed, when the liquid is arranged in a uniform thread. The most serious causes of error having been reviewed, it is possible to describe the forms of apparatus which we have used in order to avoid them.

Apparatus.

In order to obviate the uncertainty of temperature, and the last mentioned difficulty of measurement, we decided to enclose the greater part of the liquid to be examined in a thin glass bulb. Barus, indeed, had seen the advantage of this arrangement, but he was unable to prevent the fracture of the bulb under comparatively small pressures. In order to obviate this difficulty, we surrounded the bulb with mercury, and subjected the exterior to the same pressure as that applied to the liquid within. The balancing of pressure prevented the bulb from bursting, and the great thermal conductivity of mercury soon estab-

[1] Amagat, Am. Chem. Phys. (6), 22, 95 (1891).

[2] Bull. U. S. Geolog. Survey, No. 92 (1892).

lished constancy of temperature. The change of volume could be sharply read in a connecting capillary tube.

In order to determine the changes of volume suffered by this bulb and tube under various pressures, we used mercury as a standard substance, depending upon the very satisfactory results of Amagat[1] for our knowledge of its absolute compressibility. The results are carefully stated below in such a way that if any error is discovered in the compressibility of this standard substance, the more accurate value may be easily applied. It will be seen that when the absolute compressibility of a single substance is once accurately known, the reference of all other substances to it becomes a very simple matter. It is to be hoped, therefore, that many investigators will determine by many methods the absolute compressibility of mercury, a substance which for several reasons forms an exceedingly convenient standard. We propose ourselves to do this in the future; but for the purpose of this paper the value of Amagat is quite certain enough.

The apparatus thus constituted demands a stout envelope around each end of the bulb tube, with a free space of capillary tube between. The lower of these two envelopes consisted of the compressing barrel of the admirable Cailletet machine made by the Société Genevoise for liquefying small amounts of gas. In our arrangement the free space of capillary tube was visible through an oval opening or window in the brass support which carried the upper envelope. This upper envelope in turn was closed by a heavy steel screw cap with an attached tube for transmitting the pressure. The capillary was cemented into each envelope by means of marine glue, and was calibrated with suitable care.

Because the use of this apparatus was subsequently abandoned, further description of it is unnecessary. We are indebted to Mr. Frederic Bonnet, Jr., for assistance in this part of the work.

While the device overcomes the difficulties which it was expected to overcome, three other causes of trouble still remained. These are, the mutual solubility of the liquids at the point of contact in the capillary tube, the adhesion of the compressed liquid to the wall of this tube from which it has retreated, and the frequent fracture of the free portion of the tube at pressures of even less than four hundred atmospheres.

In our first experiments with bromine, we used water saturated with this substance as the containing or compressing liquid; but we

[1] *Loc. cit.* The value found by Amagat is 0.000 003 92 if the unit of pressure is the atmosphere, or 0.000 003 80 if the unit is the kilogram per sq. cm.

had no knowledge of the change of solubility of bromine in water with change of pressure. Moreover, the bromine in the vicinity of water must have been saturated with the latter substance; hence the result was at best an approximation. When the bulb was in the upper receptacle, the force of gravity assisted the adhesion of the bromine to the walls of the tube, and the adhering bromine was clearly visible; but when the bulb was below, gravity had the contrary effect, and the adhesion became less serious.

In the first position, a pressure of 50 kilograms per square centimeter was found in one tube to cause an apparent compression of 0.284 per cent. of the volume of the bromine and 0.007 per cent. of the volume of the mercury. Thus the difference between the compressibility of mercury and bromine was found to be 0.0000554, the unit of pressure being taken as a kilogram per square centimeter. Adding to this the compressibility of mercury, 0.00000380, the value 0.0000592 is obtained for that of bromine, a value probably too high for the reasons already named.

Other trials, with a wider tube and with the bulb in the lower envelope, diminished the error due to the adhesion of bromine. Thus the percentage change of volume for pressures of 50, 100, and 150 kilograms per square centimeter respectively were found to be 0.272, 0.538 and 0.797 per cent. for bromine, and 0.011, 0.022 and 0.033 per cent. for mercury respectively. These data lead to the following values of the compressibility of bromine — from 0 to 50 atmospheres, 0.0000582; from 50 to 100 atmospheres, 0.0000576; and from 100 to 150 atmospheres, 0.0000570. The temperature was 17° C. As will be seen later, these values are not far from the true ones; and they are consistent enough to show a steady decrease of compressibility with increasing pressure, which seems to be the universal rule.

The experience thus gained led to the devising of a new method retaining all the advantages, and at the same time obviating all the disadvantages of the previous procedure. In this new method, the bromine, instead of being in contact with any other fluid, was enclosed hermetically in a very thin, flat flexible glass bulb, containing no other substance. The decrease of volume in this bulb upon compression was determined as if it were a homogeneous solid, by compressing it under mercury in a suitable vessel to be described later. Allowance is easily made for the change in volume of the mercury and glass, if the containing apparatus has been properly tested full of mercury in the first place.

Since the bulbs were so thin as to collapse under a pressure of less

than the quarter of an atmosphere, the pressure within them must have been essentially the same as that applied without. Some experience and art were needed in order to prevent these bulbs from being so thin in places as to be fractured by the buoyant pressure of the mercury; and a number of exasperating accidents occurred from this cause. It is perfectly possible, however, to make a glass bulb, containing several cubic centimeters, which will change under pressure by five per cent. of its volume and yet be strong enough to endure immersion in mercury. Our experiments were made with such bulbs. The diagram (Fig. 1) represents one of them. Their flattened sides were best produced by well directed heating after the cylindrical shape had been first attained.

FIG. 1.

For the purpose of filling, the neck of the bulb was at first drawn down stoutly in the fashion indicated by the dotted lines in Fig. 1. After having been filled by means of a capillary funnel tube, the bulb was packed in ice and water. When the liquid within had contracted so much as to leave the narrowed part far above the meniscus, this narrow portion was drawn out to a very fine point, the bulb itself being shielded from the heat by asbestos. Upon warming the bulb through a degree or two this capillary point was at once filled with liquid, and was then sealed by fusion, usually without enclosing a visible trace of air, and always without enclosing a measurable trace. The weight of the glass in the bulb was always determined, either by subtracting the drawn-off tip from the total original weight, or else by weighing the glass fragments after the experiment. The weight of the enclosed liquid was obtained by weighing the sealed bulb, and subtracting from this the weight of the glass.

The bulb having been filled at two or three degrees above zero the expansion of the liquid within caused the walls of the vessel to swell outward at 20° ; and thus the possibility of compression of the bulb at ordinary temperatures was greatly increased. In the calculations the slight compressibility of the glass of this bulb was taken into account.

It is now necessary to describe the apparatus containing mercury by means of which the decrease in volume of the bulb was found. This apparatus, pictured in Fig. 2, consisted simply of a wide short test tube, with a very well ground hollow stopper terminating above in a fine funnel tube provided with a downward pointing platinum wire. For the sake of clearness this apparatus will always be called the *glass*

jacket. It was filled with the liquid metal, and the change in volume for different pressures was measured very simply by placing the whole jacket under the liquid in the Cailletet barrel, adding successive weighed portions of mercury, and noting each time the pressure needed just to break and then again make the electrical connection between the meniscus and the platinum point. The electrical method of indication has often been used for similar purposes, especially by Barus and Amagat; but never in exactly this way. If the platinum wire is very finely pointed, the fine tube around it about 1.5 mm. in diameter and the meniscus perfectly clean, the indications of this instrument are surprisingly constant and trustworthy. Even with a substance no more compressible than mercury it is easy to be certain of the necessary pressure within one atmosphere—a very small fractional error in many hundred atmospheres. The pressure at which the connection was made was taken as the true point, rather than that at which the connection was broken, since there is sometimes a slight adhesion between the point and the mercury under the last named circumstances. Often, however, the making and breaking occurred within an atmosphere's pressure of one another.

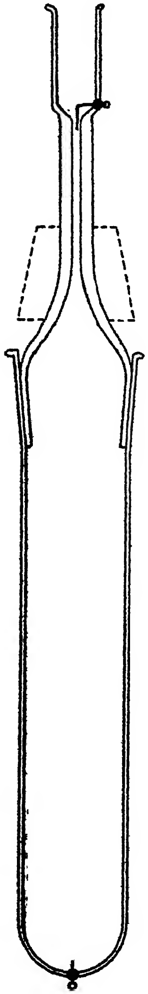


FIG. 2.

If the fine tube is larger than 1.5 mm., the sensibility of the instrument is reduced; if it is much less than 1.5 mm., drops of mercury are likely to be caught and held by the wire.

The most serious possible cause of error arises, however, from the faulty fitting of the ground stopper of the glass jacket. If a poorly ground stopper be used, the mercury during the process of compression is forced into the tiny interstices between stopper and tube — a complication which makes the compressibility of the liquid seem slightly greater than it is. This difficulty may be obviated wholly by always wetting the ground surfaces with a minute drop of water or some other liquid, thus displacing all the air, and preventing the ingress of mercury. The infinitesimal variations in the compression of this practically constant drop of lubricating liquid are quite too small to produce any perceptible effect, and successive trials always yield the same result.

The filling of the simple apparatus was conducted in the following manner. The lower tube of the glass jacket was filled with mercury, a single drop of water was placed on its surface, and the stopper was carefully inserted and tied down with stout string passed over a rubber shoulder. The latter, used to give needed elasticity, is indicated by dotted lines in Fig. 3. The cavity in the stopper was filled with mercury from above by means of a capillary funnel tube, as far as the point of the platinum wire; and the mercury surface was separated from the mineral oil of the Cailletet compression barrel by water, which filled the upper part of the funnel tube. As already stated the meniscus must be perfectly clear and free from oil, otherwise its curve is irregular. In order to conduct away the heat of compression and to make the lower electrical contact, mercury was poured around the outside of the lower two thirds of the glass jacket.

The upper platinum wire was connected with an insulated wire running through a capillary glass tube sealed into the upper movable part of the Cailletet apparatus, and the contact was detected with the help of a feeble cell and a delicate index-galvanometer. The apparatus being tightly screwed into place, pressure was applied until the circuit was broken — a condition which showed that the mercury had been compressed until its meniscus had fallen below the platinum point. The mercury was kept at this point for twenty minutes, or until the pressure readings became constant. The heating effect of the compression was considerable; but the inner jacket being immersed in mercury, the heat was quickly conducted away to the large surrounding thermostat, kept constant to within 0.01° C., in which the Cailletet barrel was immersed. An idea of the speed of this equalization of temperature can be gained from the following table. Here the pressures corresponding to the break of electrical contact are given at various times, beginning with the time of the first quick compression:

Time.	Pressure at which Contact was Broken. kg./cm^2.
0 sec.	410
20 "	352
40 "	345
1 min.	340
2 "	335
3 "	331
4 "	327
5 "	326
10 "	326
15 "	326
20 "	326

Constancy in the readings was reached in five minutes. The glass jacket in this case contained a bulb of chloroform immersed in the mercury.

The quantity of mercury in the glass jacket was usually so adjusted that the first constant pressure reading was between fifty and one hundred atmospheres, and this first reading was taken as the starting point of the determination. Minute air bubbles were thus disarmed of possible injurious effect. As already suggested, a weighed quantity of mercury was now added through the funnel tube (see Fig. 2) and pressure again applied. The added pressure necessary to break the electrical circuit corresponded to the volume of the extra mercury introduced. This process was repeated until the highest pressure was reached, and thus were found the points on a curve which depicts the difference between the compressibilities of mercury and glass. Only in the most accurate work is it necessary to consider the compression of the small extra volumes of mercury introduced, since the omission of this correction causes an error of only 0.04 of one per cent. for every hundred atmospheres.

If now there is introduced beneath the mercury the substance whose compressibility is to be determined, and a new curve is found in the same way, it is evident that the differences between these two curves represent the differences between the compressibility of the new substance and an equal volume of mercury.

A typical series may better serve to make clear the method of observation and calculation. The first process is the calibration of the glass jacket with mercury already described. The pressure readings given below were taken after successive additions of mercury, the whole apparatus being filled with this liquid.

Initial reading: Circuit made 37, 37, 37, 37, 37 kg./cm^2. Circuit broken, 40, 39, 39, 39, 39 kg/cm^2.

After adding first quantity of mercury, = 0.1020 gram. Circuit made 254, 255, 254, 254, 254 kg./cm^2. Circuit broken 257, 256, 256, 256, 256 kg./cm^2.

After adding second quantity of mercury, = 0.0998 gram. Circuit made 476, 476, 476, 476 kg./cm^2. Circuit broken 478, 478, 478, 478 kg./cm^2.

After adding third quantity of mercury, = 0.0660 gram. Circuit made 632, 634, 634, 634, 634 kg./cm^2. Circuit broken 636, 636, 636, 636, 636 kg./cm^2.

A bulb filled with bromine was now put into the jacket; the remaining space was filled with mercury and a new series of pressure

readings taken. The weight of the bromine was 7.502 grams, while the thin containing bulb weighed only 0.72 gram.

Initial reading: Circuit made 68, 68, 68, 68, 68 kg./cm². Circuit broken 70, 70, 70, 71, 69 kg./cm².

After adding first quantity of mercury, = 0.3338 gram. Circuit made 223, 223, 223, 223 kg./cm². Circuit broken 227, 225, 225, 225 kg./cm².

After adding second quantity of mercury, =0.3357 gram. Circuit made 391, 392, 392, 392, 392 kg./cm². Circuit broken 393, 394, 393, 393 kg./cm².

After adding third quantity of mercury, = 0.3259 gram. Circuit made 566, 565, 565, 565, 565, 565 kg./cm². Circuit broken 567, 567, 569, 567, 568, 567 kg./cm².

From the results with mercury a curve is plotted with pressures as abscissas and total weights of mercury as ordinates. The ordinates on this curve which correspond to the pressures found in the series with bromine evidently represent the weights of mercury which are to be subtracted from the weights actually added in the bromine series in order to obtain a basis for calculating the difference between the volume change of the bromine and the change in an equal volume of mercury.

The equation for calculating the average compressibility between the pressures P_1 and P_2, *i. e.*, the volume change for a unit of the original volume subjected to an increase of a unit of pressure, is obviously:

$$\beta = \left(\frac{(w - w')(1 - P_1\beta')}{13.546} + \frac{w''}{d}(P_1 - P_2)(\beta' - \beta'') \right) \frac{D}{W(P_1 - P_2)} + \beta' \qquad (1)$$

where

β, β', and β'' equal respectively the average compressibilities of the substance studied, mercury, and glass;

w and w' equal respectively the two weights of mercury in the two series above described corresponding to the given change of pressure $P_1 - P_2$.

w'' and W respectively the weights of the thin glass bulb and the substance studied;

d and D the densities of glass and of this substance, and,

13.546 the density of mercury at 20°.

The value $\beta' - \beta''$ is obtained, as will be seen later, directly in the

first or mercury series by dividing the added weight of mercury by the product of the total weight of mercury and the added pressure.

$$\beta' - \beta'' = \frac{w'}{W'p}. \qquad (2)$$

For the absolute value of β'; we have had to depend upon Amagat's work, as already stated — an investigation that gives this value only as far as fifty atmospheres. Since the magnitude of β' is never greater than 0.00000380, a slight variation in it with the pressure can be of no serious importance in the present work. In order, however, to make as easy as possible the correction of our results in case our assumed value of β' is in error, there is recorded below not only the value β, but also the value $\beta - \beta'$. This quantity $\beta - \beta'$ relies essentially upon our own work, and at any time the compressibility β may be found from it by adding the most probable compressibility of mercury.

The same apparatus serves for determining the compressibility of solids; but with liquids which do not attack mercury a still simpler device may be used. The thin walled bulb may be dispensed with, and the jacket itself used to contain the liquid. In this case a doubly bent tube must be attached above, in order to contain the mercury necessary for making electrical contact. The apparatus thus assumes the form shown in Fig. 3, the stopcocks being affixed to facilitate filling. For the most accurate work it would be better to omit these stopcocks, and to fill the jacket by exhausting the air; because the stopcocks are liable to leak unless very well ground, and their presence introduces a slight uncertainty due to the small amount of liquid contained in their channels. In our experiments this small volume, amounting to only 0.002 of the whole, could be safely neglected. It is well not to heat the glass to a high temperature, during the filling, because of its well-known volume lag. On the other hand, we have as yet been unable to detect any appreciable volume lag on compression. This is shown by the fact that series of experiments made by *taking out* mercury after the attainment of high pressure give results identical with those obtained by gradually *adding* mercury.

After being thoroughly cleaned this jacket was filled with mercury and the stopcocks were closed. The mercury was arranged at a level slightly above the lower point of the upper wire and the funnel tube above was filled with pure water as before.

The jacket was placed in the Cailletet barrel, and the pressures corresponding to successive added portions of mercury were found in the way already described. Thus the mercury curve was determined.

The greater part of the mercury was now withdrawn, and the residue, filling the U-tube at least, was weighed with the glass. Subsequently the liquid under investigation was drawn in, completely displacing the air; and finally the apparatus, after external drying, was weighed again. Thus was found the weight of the liquid to be compressed.

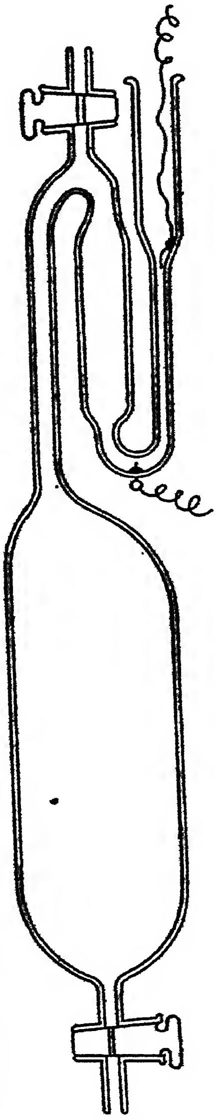


FIG. 3.

The jacket was now placed once more in the Cailletet barrel, and once more the pressures corresponding to successive added portions of mercury were found. These new readings define the curve of compressibility of the liquid and the residual mercury. The differences between the weights of mercury added, for any given change of pressure, as found on the two curves, give by simple calculation the differences between the compression of the given volume of liquid and the same volume of mercury, hence the compressibility is easily computed with the help of the following equation, in which the symbols have the same significance as before.

$$\beta = \frac{(w - w')(1 - \beta P_1)D}{13.546\, W(P_1 - P_2)} + \beta'. \qquad (3)$$

COMPRESSIBILITY OF MERCURY AND GLASS.

Since both the difference between the compressibility of glass and mercury and the absolute compressibility of mercury enter into the equations, it is important at the outset to determine these quantities as definitely as possible. Accordingly several careful series of experiments were made. Because the change in the capacity of a hollow glass vessel under compression is equal to the change in the same volume of solid glass, the value $\beta' - \beta''$ may be determined by compressing mercury in the jacket already described. Three of these jackets, numbered I, II and III, were of the type suitable for solids depicted in Fig. 2, while the fourth was of the type designed for liquids, depicted in Fig. 3. In the table below the actual figures found with these four jackets are given, and in the third column the added weights of mercury w' are all divided by the total

weight of mercury W' in order to reduce all the results to a comparable basis, namely, the results which would have been obtained if the jackets had each held only a gram of the metal. The fourth column contains this quantity with an added quantity a_n constant with each series. This a_n is necessary to reduce these measurements beginning at various pressures to the same starting point. The method of doing this is explained in the following paragraph.

COMPRESSION OF MERCURY IN GLASS.

Number of Jacket.	Total Weight of Mercury at 20° C.	w' = Weight of Added Mercury.	$\frac{w'}{W'}$	$\frac{w'}{W'} + a_n$	Pressure Corresponding.
	grams.	milligrams.	milligrams.	milligrams.	kg./cm².
I.		0	0	$0.055 = a_{\text{I}}$	37
	328	102.0	0.311	0.366	254
		201.8	0.615	0.670	476
		267.8	0.814	0.869	634
	437	0	0	$0.143 = a_{\text{II}}$	98
II.		153.2	0.351	0.494	347
		273.2	0.623	0.765	547
	308.6	0	0	$0.176 = a_{\text{III}}$	122.0
III.		106.6	0.345	0.521	369.5
		166.9	0.541	0.717	518
IV.	291.6	0	0	$0.116 = a_{\text{IV}}$	80
		118.9	0.407	0.523	365

The results are best compared by graphic method, hence a diagram is given herewith (Fig. 4). The portion of the curve below 37 atmospheres is extrapolated (a proceeding which is indicated by the dotted line) and the second, third and fourth series are begun intentionally on the curve of the first. a_n is in each case the ordinate corresponding to the first pressure of each series. Hence the lowest four points are fixed arbitrarily and the agreement of the results is shown only by the seven points at the pressures above 200 atmospheres. This agreement is nevertheless close enough to satisfy the most exacting requirements of the present work. The third series of experiments was made by Mr. Frederick Bonnet, Jr.

This curve represents various values of $\beta' - \beta''$, or the differences between the compressibilities of glass and mercury at different pressures, both being at 20°. After having been plotted several times on a large scale, the most probable values for this quantity were found from the averages to be those recorded on page 20.

Thus there is a steady decrease in the value of $(\beta' - \beta'')$ as the pressure decreases. Without further data it is impossible to determine how

but fortunately Amagat's results enable us to decide. He found by measuring linear compression that glass possessing below 500 atmospheres an average compressibility of 0.00000225 decreased in com-

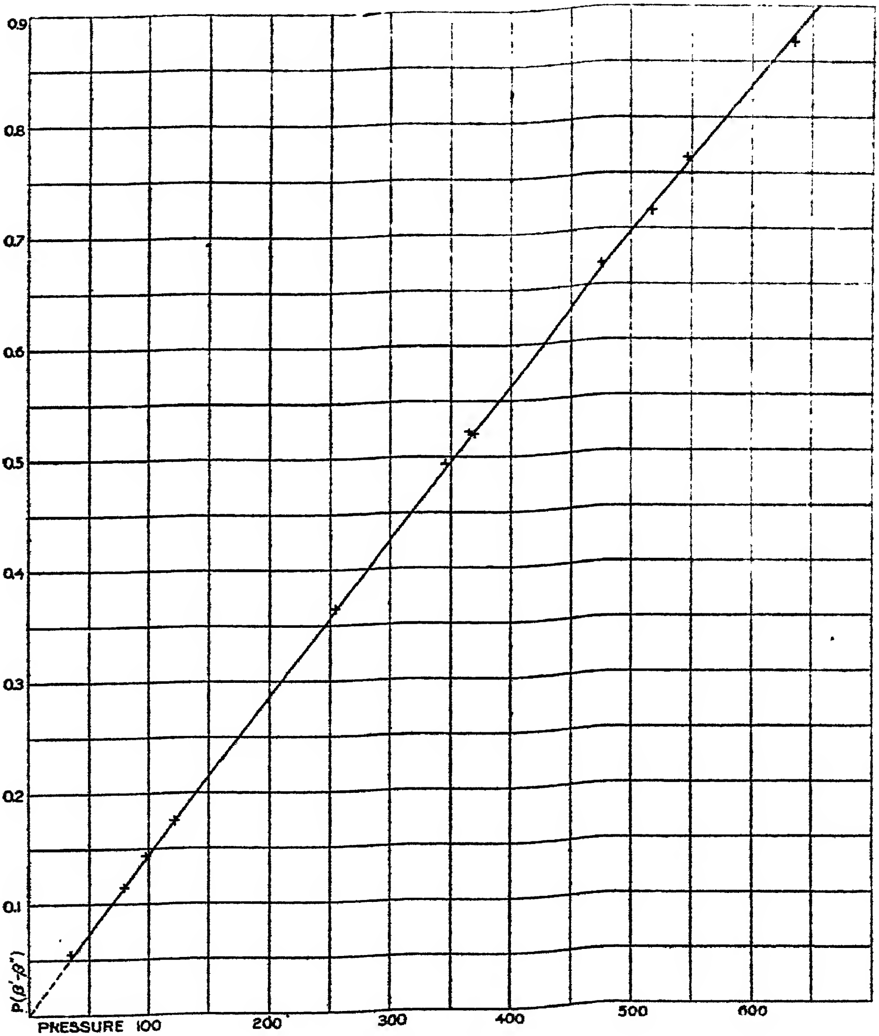


FIG. 4.

pressibility only a unit in the last decimal place between 500 and 1,000 atmospheres. Hence the compressibility of glass is almost a constant, and its curve with increasing pressure practically a straight line.

Range of Pressure.	$(\beta' - \beta'')\,10^6$.	Probable Values of Compressibility of Mercury. (See Explanation Below.)
kg./cm².		$\beta'.(10^6)$.
0–100	1.48	3.80
100–200	1.43	3.75
200–300	1.40	3.72
300–400	1.37	3.69
400–500	1.32	3.64
500–600	1.28	3.60

Therefore the progressive change in the value $\beta' - \beta''$ given above must be due to the mercury alone, if the pressure readings were exact.

The quantity β'', while constant for any one kind of glass varies considerably with different kinds of glass. Amagat found values ranging from 0.000 002 2 to 0.000 002 5.

In our case the constant β'' is easily found by subtracting the first value of $\beta' - \beta''$ from the compressibility of mercury 3.80×10^{-6} found by Amagat. $\beta'' = \beta' - (\beta' - \beta'') = (3.80 - 1.48)\,10^{-6} = 2.32 \cdot 10^{-6}$. This result corresponds well with Amagat's.

It is possible now to obtain a close approximation to the values of β' for pure mercury by adding the constant β'' to the values $\beta' - \beta''$.

The values given in the last column of the table are computed in this way. They are not certainly exact, but will amply serve the purpose of this paper.

Unfortunately Amagat does not state the temperature at which his value for mercury 0.000 003.8 was found. Accordingly, by comparing the behavior of a jacket filled with mercury at 0° with one at 20°, we sought to trace the possible magnitude of the uncertainty.

A change in pressure from 155 to 563 kilograms per square centimeter required an additional weight of mercury of 0.2486 gram or 0.01830 milliliter at 0°, while the same change in pressure required 0.2475 gram or 0.01828 milliliter at 20°. These two volumes are almost exactly identical, hence $\beta' - \beta''$ does not change sensibly with the temperature. In other words, the compressibility of glass and mercury change by the same actual amount in 20°. But Amagat found that the compressibility of glass changes about 3 per cent. for 100° C.—or about 0.000 000 014 for 20°. Hence if the compressibility of mercury at 20° is 0.000 003 80, the compressibility at 0° must be 0.000 003 786. This difference of one third of one per cent. is too small to produce any essential effect on our work, causing for example only an uncertainty of one fiftieth of one per cent. in the compressibility of bromine.

While the value of $\beta' - \beta''$ varies perhaps from 1.48×10^{-6} to 1.28×10^{-6} in a range of 600 atmospheres, it is nevertheless sufficiently constant to make possible a simplification of equation (1) on page 15 without the introduction of appreciable error. Noting that $\beta' = 0.0000038$, $\beta' - \beta'' = 0.0000014$ and $d =$ the density of glass $= 2.5$ we have

$$\beta - \beta' = \left(\frac{(w - w')\ (1 - \beta' P_1)}{13.55} + \frac{0.0000014 w''\ (P_1 - P_2)}{2.5}\right) W \frac{D}{(P_1 - P_2)}. \qquad (4)$$

Since both $\beta' P_1$ and the second term within the parentheses are very small, the value $(1 - \beta' P_1)$ may be removed outside of the parentheses without introducing appreciable error.[1] The equation thus becomes:

$$\beta - \beta' = [w - w' + 0.0000076\, w''\ (P_1 - P_2)] \frac{D\ (1 - \beta' P_1)}{13.55\ W\ (P_1 - P_2)}. \qquad (5)$$

This equation was used in calculating all the results. When the inner thin glass bulb was omitted, in the case of liquids not attacking mercury, w'' becomes zero and the third term within the first parentheses drops out. The equation then assumes the form of equation (3) on page 17.

The value of w' used in the equation above must of course correspond to the same range of pressure $(P_1 - P_2)$ as that observed in the case of w. The value is easily found from equation (2).

$$w' = W' P_1 (\beta' - \beta'') = W' (P_1 - P_2)(\beta' - \beta'') \text{ where } P' = P_1 - P_2.$$

The value of $\beta' - \beta''$ also must correspond to the given range of pressure. This last designation is necessary because $\beta' - \beta''$ changes in value with changing pressure, as is shown on page 20. w' may also be found directly from the results given on page 18 by graphic interpolation, or from the diagram of $\beta' - \beta''$ by multiplying the ordinate value corresponding to the difference between two pressures by W'. All these methods give of course essentially the same results; they were used to verify one another in the tables given below.

Among the other quantities involved in the equation, the volumes, being found by weighing quantities of mercury determined by the

[1] For a table of formulæ giving the permissible abbreviations of equations involving small quantities in the presence of large ones, the reader is referred to Nernst and Schönfliess, Math. Behand. der Naturwiss., p. 303 (1895).

exceedingly sensitive electrical contact, can be estimated with great accuracy. For the pressures, on the other hand, we have had to depend chiefly upon the hydraulic dial gauge made and guaranteed by Schaeffer and Budenberg. In view of the extensive experience of these manufacturers and the fact that the gauge is vouched for by the Société Genevoise it seemed hardly possible that we could improve upon the accuracy of their work. The gauge registers as far as a thousand atmospheres, and has only a very small temperature coefficient, according to their testimony and our careful trial. We tested this by means of our new liquid manometer, described on page 41, keeping the latter constant in temperature and varying the temperature of the dial gauge. The temperature of the room used for the experiments varied ordinarily but little from 20°, hence no trouble could have arisen from change of temperature, even had the coefficient been considerable.

Several other indications point to the accuracy of the gauge. For example, the great regularity to be seen in the various curves, particularly in that representing $\beta' - \beta''$, points toward consistency in the indications.

A number of comparisons of the gauge with known weights placed at the end of the lever arm of the press confirmed to some degree this conclusion. In order wholly to eliminate friction, and thus test this method more thoroughly, a rotary piston might have been provided. This change would however have involved a fundamental dismantling of the apparatus, an act which at present we were not willing to perform. Yet another indication of the accuracy of the gauge is found in the essential agreement of our work upon water, described later, with the work of others.

After the work was completed, our gauge was returned to Schaeffer and Budenberg, in order to be thoroughly tested anew. Their report was very satisfactory, indicating inessential errors in the lower part of the scale, and giving the error at 500 atmospheres as only 0.5 atmosphere.

Whatever may have been the error of the gauge, the results are accurate relatively to one another; moreover, they may be easily corrected at any future time with the help of the liquid manometer already mentioned.

In view of the facts above stated, it seems certain that the possible inaccuracies of the gauge must be so small as to affect only the second differential coefficient, and not the average value of the compressibility. Hence even if the possible errors in the gauge were never found, the following results would be significant.

The substances whose compressibilities we have determined are bromine, iodine, chloroform, carbon tetrachloride, bromoform, phosphorus and water, while from the results we may also obtain the value for glass and a qualitative indication of the compressibility of liquid chlorine. In every case the temperature was 20°. Further details are best discussed under the individual experiments.

Bromine.

Two samples of bromine were used. The first specimen (used in all but the last series) was prepared by the usual calcic bromide method of Stas. It was subjected to an initial distillation, was dried by means of phosphorus pentoxide, and twice redistilled, but was not wholly free from dissolved air. Sample two (2) was an especially pure specimen which had been prepared by Richards and Merigold[1] for their work on the atomic weight of uranium. It was dried over phosphorus pentoxide and redistilled. The air was expelled by boiling just before use.

The equation for the calculation of the compressibility shows that it is necessary to know accurately the specific gravity of the substance under examination. Thorpe[2] found as the specific gravity of bromine at 0° (water at 4° being the standard) the value 3.1882. Pierre[3] found, with the same standard and temperature a value, 3.18721. He found also that between − 7° C. and 60° C. the expansion formula is

$$V = 1 + .001\,038\,18\,t + .000\,001\,711\,4\,t^2 + .000\,000\,005\,447\,t^3.$$

The average of the values of these two experimenters, viz., 3.1877, was taken as the density (0°/4°), and with this as a basis the value at 20° C. was obtained by the use of Pierre's formula. The result is 3.120 (20°/4°), and this value was used in the calculations below.

There are given below the essential data and results of five series of experiments upon bromine, made with two different portions of material and two different jackets.

In series 1, 2, 3 and 4, the weight of bromine was 7.504 grams, corrected to vacuum, and the containing thin bulb weighed $w'' = 0.72$ gram. In series 5 the bromine (the second sample, free from dissolved air) weighed 12.649 grams (in vacuum) and the glass bulb weighed $w'' = 1.10$ grams.

[1] Proc. Am. Acad., 37, 387 (1902).
[2] Journ. Chem. Soc., 37, 172 (1880).
[3] Ann. de Chim. et Phys. (3), 20, 45 (1847).

DATA FOR COMPRESSIBILITY OF BROMINE. (20°C., HYDROGEN SCALE.)

No. of Series.	No. of Jacket.	Observed Pressure $=P$ in kg./cm².	Actual Mercury Added $=w$.	Mercury Added in Absence of Bromine $=w'$ $=(P_1-P_2)\times(\beta'-\beta'')W$.	Correction for Glass Bulb $=0.0000076\,w'(P_1-P_2)$.	Total Change of Volume of Bromine Minus that of Mercury $(\beta-\beta')P$. Per cent.
		46	0	0	0	[0.273 $=a_1$]
1	I	226	0.391	0.085	0.0010	1.216
		442	0.818	0.182	0.0021	2.232
		624	1.147	0.259	0.0031	3.007
2	I	68	0	0	0	[0.392 $=a_2$]
		223	0.334	0.073	0.0009	1.195
		392	0.669	0.150	0.0017	1.991
		565	0.995	0.224	0.0027	2.765
3	I	60	0	0	0	[0.350 $=a_3$]
		206	0.320	0.069	0.0008	1.121
		369	0.649	0.143	0.0017	1.910
		543	0.983	0.219	0.0027	2.700
4	II	47	0	0	0	[0.278 $=a_4$]
		143	0.242	0.059	0.0005	0.844
		251	0.486	0.127	0.0011	1.384
		375	0.742	0.202	0.0017	1.940
		496	0.992	0.273	0.0024	2.492
5	II	69	0	0	0	[0.400 $=a_5$]
		110	0.157	0.025	0.0003	0.640
		162	0.334	0.058	0.0008	0.905
		253	0.643	0.113	0.0014	1.366
		356	0.984	0.176	0.0034	1.876

As will be observed, the pressures of the starting points of these five series vary considerably. In order to bring them to comparable conditions, we resorted to the following method: The first series, that with the lowest starting point, was plotted with "total percentage changes of volume of bromine minus those of mercury" in the direction of ordinates and the pressures corresponding to these volume changes as abscissas. The portion of the curve below 46 atmospheres was extrapolated. Let us call this curve *one*. To plot the results of series 2, for example, we found the point on curve *one*, which corresponded to the initial pressure (68) of (2); and its ordinate gives the amount a_2 which must be added to the ordinates calculated for higher pressures before the loci of series 2 could be plotted.

In other words a_n is the volume, constant within each series, which must be added to each member of the series in order to reduce them all to the same origin. It is found exactly as in the case of mercury already discussed, being the ordinate corresponding to the initial pressure of each series, measured on the curve of Series I. By adding this quantity a_n, all the series are superposed at their lowest pressures, and the resulting curve begins at the origin of pressure and

of volume change. As has been said, that part of the curve below 46 atmospheres is extrapolated, but an error occurring in it could have no effect on the curve above, for this depends entirely upon the actual observations. Since the calculation is somewhat complicated, it may be well to state that it was performed from beginning to end by each of the authors independently on different kinds of coördinate paper, with precisely similar results. The plot being 40 centimeters high and 33 centimeters wide, a considerable degree of accuracy was obtained. It was easy to distinguish 0.02 centimeter or 1/2000 of the maximum values.

Thus the quantity given in the last column of the preceding table, plotted in the direction of ordinates on the curve marked bromine in the chart is

$$[w - w' + 0.000\,007\,6w''(P_1 - P_2)]\frac{D(1 - \beta' P_1)}{13.546\,W} + a_n = (\beta - \beta')P_1.$$

From the curve it is at once clear that the compressibility decreases rapidly as the pressure increases. In the table below, the values of $\beta - \beta'$ are given for each hundred kilograms per square centimeter expressed in fractions of the original volume. The value between 0 and 100, being partly extrapolated, is enclosed in brackets. These values were taken directly from the curve.

COMPRESSIBILITY OF BROMINE AT 20° C.

Range of Pressure (kg./cm².)	$(\beta-\beta')10^{-6}$.	Compressibility of Bromine $= \beta$.
0–100	[57.5]	[0.000 061 3]
100–200	52.5	0.000 056 3
200–300	48.0	0.000 052 7
300–400	46.5	0.000 050 2
400–500	44.5	0.000 048 1
500–600	42.8	0.000 046 4

Thus the compressibility of bromine is about sixteen times as great as that of mercury at low pressures. The difference of temperature (3°) accounts in part for the difference between these results and the preliminary ones given on page 10.

IODINE.

In order to prepare suitable material, "chemically pure" iodine was mixed with pure potassium iodide, the two being finely ground, and the iodine was sublimed, twice in succession.

As before, it was important to know accurately the specific gravity of the substance at 20°. Gay Lussac[1] found the value 4.948 (17°/17°) and this reduced to (17°/4°) gives a value 4.942. Billet[2] found the following values:

Temperature	40.3°	60°	79.6°	89.8°
Specific gravity............	4.9173	4.886	4.858	4.841

but unfortunately it is not evident whether these values are based on water at 4°, or at some other temperature. We can, however, obtain the inclination of the curve from his results and plot a parallel curve passing through the value obtained by Gay Lussac. The density thus obtained is 4.938 (20°/4°). The value used in the calculations was 4.94.

The method employed for determining the compressibility of iodine was essentially that used in the bromine experiments. The question of the isolation of the iodine from contact with the surrounding mercury was, however, even more perplexing than with bromine. The problem was finally solved according to the following method. Two small bulbs, similar to those used with bromine, were prepared (*A* and *B*). Into *A* was put a saturated solution of iodine in water, a few wisps of glass wool, and a small quantity of solid iodine. Into *B* was put a saturated solution of iodine in water and a large quantity of iodine. Both were sealed and subjected to quantitative compression. The glass wool served to hold the small bits of iodine at various positions throughout the solution, thus facilitating the speed of any possible shift in the solubility-equilibrium when the pressure changed.

If there are a grams of water and b grams of iodine in A, and c grams of water and d grams of iodine in B, and if volume change of A under pressure is m and of B for same pressure is n we have the following relationship:

$$\frac{a}{c} = \frac{a+b}{c+\delta} = \frac{m}{x},$$

where δ is a quantity of iodine which bears the same relation to c that b bears to a (that is, $a/b = c/\delta$), and x is the volume change of the water c in tube B plus the volume change of a small quantity of iodine, δ. Evidently, then, $(n - x)$ represents the volume change of the quantity of iodine $(d - \delta)$. This method is, of course, applicable in all cases where the solid under consideration is attacked by

[1] Ann. de Chim., 91, 5 (1814).

[2] Jahresbericht, (1855) 46.

mercury. There are two distinct reasons for the use of mercury instead of the direct use of the neutral liquid in the outer jacket — first, because the transmission of the heat of compression to the surrounding water when mercury is used is quick and certain, and second because the compressibility of mercury is so small that any slight change in volume due to a slightly different placing of the stopper cannot influence the results. With more compressible liquids the error thus introduced might be considerable.

The special advantage of the method in connection with iodine lies in the fact that it obviates all possible error due to a change in the solubility of iodine in water with change of pressure. There are, it is true, two possible sources of error which it does not guard against: first, the solubility of water in iodine; and secondly, the change in that solubility with change of pressure. When we consider, however, the fact that liquids usually dissolve solids to a greater extent than solids dissolve liquids, and remember that iodine is soluble in water to the extent of only about one part in three thousand, it is hard to believe that either of these influences could have an appreciable effect upon the results obtained below. Moreover, since the compressibilities of iodine and water are of the same order of magnitude, the amount of water dissolved by the iodine must be great before any difference would appear in the result. In obtaining the weight of iodine and water, the method used was to weigh the bulbs full of water and iodine; then break them under a solution of potassium iodide and titrate the iodine with recently standardized thiosulphate. The glass particles were then collected, dried and weighed, and the weight of the water was found by difference. The small amount of iodine dissolved in the water was neglected as too slight to cause appreciable effect. For the purpose of standardizing the sodic thiosulphate solution, 3.080 grams of dry, recently resublimed iodine were dissolved in potassium iodide solution and diluted to a volume of 0.2509 liter. This was titrated against the approximately decinormal thiosulphate solution. The results are given below, burette corrections having been applied. As an average of three closely agreeing determinations, 44.29 milliliters of the thiosulphate solution required 25.92 milliliters of the iodine solution. Therefore one milliliter of the thiosulphate solution was equivalent to 0.007246 gram of iodine.

The total quantity of iodine in bulb *A* required 22.67 milliliters of the thiosulphate solution, therefore the weight of iodine present must have been 0.1643 gram.

The iodine in bulb *B* was dissolved in potassium iodide and diluted

to 0.2509 liter, and as an average of three closely agreeing titrations 17.32 milliliters of this solution required 45.45 milliliters of the thiosulphate solution. Therefore the number of grams of iodine in *B* was 4.7723 grams. The weights of the glass in the two bulbs *A* and *B* were respectively 0.91 and 0.97 gram, and the weights of water present in each were respectively 2.674 and 1.829 grams.

In both cases jacket II was used.

COMPRESSIBILITY DATA FOR IODINE.

Bulb A.

Series.	Observed Pressure.	Total wt. of Hg Added.	Correction for Jacket.	Correction for Bulb.	Corrected wt. of Hg Added.	m'.
6	53	0				0
	173	0.2438	0.0740	0.0008	.1706	0.464
	302.5	0.5013	0.1540	0.0017	.3490	0.950
7	90	0.0000				0
	217	0.2584	0.0783	0.0008	.1809	0.492
	302.5	0.4278	0.1313	0.0014	.2979	0.811
			Bulb B.			n'.
8	88	0				0
	233	0.2502	0.0893	0.0010	.1619	0.428
	384	0.5003	0.1813	0.0021	.3211	0.848
9	111	0				0
	248	0.2365	0.0840	0.0010	.1535	0.405
	384	0.4633	0.1670	0.0019	.2982	0.788

Under m' is given the percentage change in volume of 2.674 grams of water and 0.1643 gram of iodine minus the percentage decrease of an equal volume of mercury. (6) and (7) are two series, the first made by adding small quantities of mercury, the second by *taking out* small quantities after the highest pressure had been reached. This method of procedure is especially desirable with solids, as it will afford indication of a permanent alteration in the volume of the solid under pressure, if such alteration occurs. It also gives valuable proof of the absence of leakage from the glass jacket.

Under n' is given the percentage decrease in the volume of 1.829 grams of water and 4.7723 grams of iodine minus the percentage decrease of an equal volume of mercury. (8) and (9) are two series made as before, one by adding mercury, the other by taking out small quantities of mercury. By adding the compression of mercury, m and n are respectively obtained from m' and n'.

Making the calculation indicated in the earlier part of the remarks on iodine, we have in the equation $\delta = bc/a$, by substituting the values found,

$\delta = 0.1643 \times 1.829/2.674 = 0.1124$ gram and $(d - \delta) = 4.66$ grams.

This represents the quantity of iodine, the compression of which was measured. Its volume is 0.943 milliliters, or 0.348 of the volume of its bulb.

Now $x = mc/a = 0.684\, m$. From the values of m given under the work on bulb A the values of x were calculated and plotted as ordinates with the corresponding pressure-differences as abscissæ. This was called the *curve of x*. Then the values found in the work on bulb B were also plotted, using values n as ordinates and pressure-differences as abscissæ. The curves were both extrapolated in order to pass through the origin. In order to economize space, the curves themselves are not given here, but in the table below are given all the data needed to reproduce them. $(n - x)/0.348P$ is the compressibility of the iodine.

COMPRESSIBILITY OF IODINE.

Abscissæ (Pressures).	Ordinates. Curve of n.	Curve of x.	$(n - x)$	$(\beta - \beta')10^6$ for Each Successive 100 Pressure Units.	$\beta.10^6$
100	[0.346]	[0.300]	[0.046]	[9.6]	[13.]
200	0.680	0.590	0.090	8.9	[13.]
300	1.005	0.872	0.133	8.6	12.

Thus the compressibility of iodine is far less than that of bromine, being only three times that of mercury. This result does not pretend to any considerable degree of accuracy; the small amount of material used and the complication of the method preventing great precision. It is, nevertheless, sufficiently certain for the present purpose, and accordingly further work upon iodine was postponed.

CHLOROFORM AND CARBON TETRACHLORIDE.

These substances were next studied, with the justifiable hope that their behavior might furnish some clue as to the compressibility of chlorine. In order to purify the former material, commercial chloroform was shaken repeatedly with strong sulphuric acid and then with successive portions of water. It was afterwards dried with calcium chloride and twice distilled. During the second distillation two thirds of the product passed over between 61.2° and 61.3° C.,[1] and from this fraction the material for the compression experiments was taken.

As before, accurate knowledge of the density is needed. Thorpe[2] found for the specific gravity of chloroform the value 1.5264 at 0°/4°; and, under the same conditions of temperature, Pierre[3] found 1.5252.

[1] The barometric pressure was 759 mm. and the thermometer reading was corrected for the temperature of the projecting column of the thermometer.

Moreover Perkin[1] found 1.5008 at 15°/15° and 1.4849 at 25°/25°. These values of Perkin's reduce to 1.4993, 15°/4°, and 1.4801, 25°/4°. If the values of these three observers be plotted the interpolated value for the density at 20°/4°, is found to be 1.490.

In order to obtain the other compound of chlorine in a pure state, tetrachlormethane of commerce was twice distilled, and the fraction coming over between 76.6° and 76.8° C. (cor.) was used. This substance has a higher specific gravity than chloroform. Thorpe[2] found (0°/4°) 1.63195 and a volume increase of 2.45 per cent. at 20°. These values give 1.593 (20°/4°).

The method of determining the compressibility of these substances was precisely similar to that used in the case of bromine. The glass jacket II, containing the maximum amount of 437 grams of mercury, was used in each of the four series given below. The weight of the chloroform was 5.354 grams, hence its volume was 3.590 milliliters, while the corresponding data in the case of the carbon tetrachloride were 6.970 grams and 4.403 milliliters. The weights of the two thin bulbs were respectively 0.55 and 1.06 grams. Series 13 was obtained by taking out mercury instead of adding it. Its perfect agreement with series 12 shows that the apparatus was in excellent order.

DATA FOR CHLOROFORM AND CARBON TETRACHLORIDE.

Series.	Observed Pressure P.	Chloroform. Weight of Hg. Added.	Total Percentage. Change of Volume Minus that of Mercury $=(B-B')P$
	kg./cm².	grams.	per cent.
10	53.5	0	$0.475 = a_{10}$
	201.5	0.684	1.691
	374.5	1.398	2.938
	574.5	2.114	4.162
11	88	0	$0.775 = a_{11}$
	181	0.442	1.565
	293	0.909	2.381
	492	1.658	3.670
	637.5	2.167	4.537
	Carbon tetrachloride.		
12	56	0	$0.499 = a_{12}$
	159	0.578	1.367
	250	1.063	2.093
	324	1.443	2.657
	410	1.839	3.237
13	248	1.048	$2.068 = a_{13}$
	410	1.839	3.237

This table contains all the data, in addition to the previously recorded figures, necessary for computing the compressibilities of the

[1] Journ. Prakt. Chem. (2), 32, 573 (1885).
[2] Journ. Chem. Soc., 37, 198 (1850).

two liquids. The last column, precisely similar to the corresponding column in the preceding data concerning bromine, gives the total change of volume in milliliters of 100 milliliters of liquid, caused by the application of each pressure, minus the total change in volume of the same volume of mercury caused by the same pressure. The corresponding curves are plotted in the diagram Fig. 5. From the average of several large plottings of this kind on two varieties of coördinate paper, the values of the compressibilities of the two liquids contained in the following table were obtained.

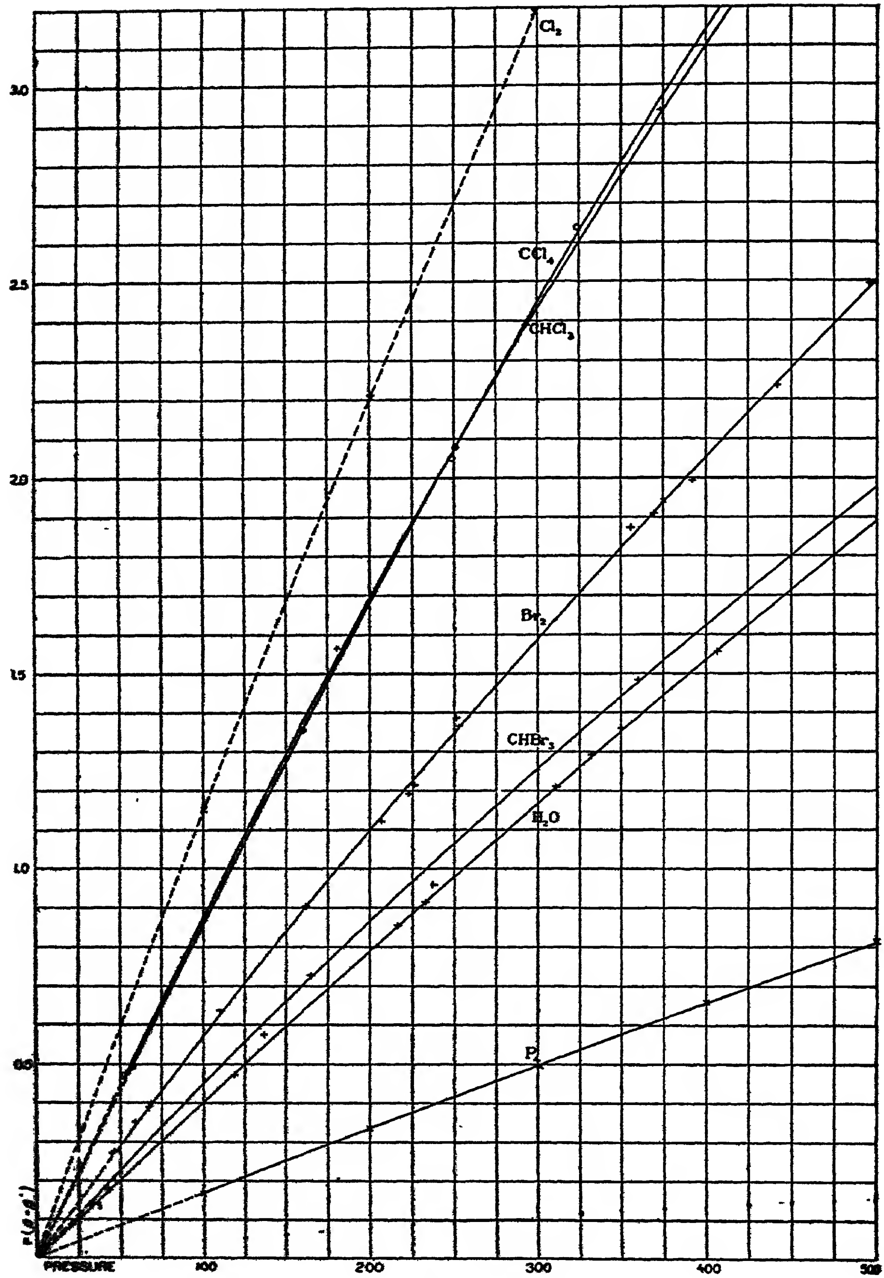
COMPRESSIBILITIES OF CHLOROFORM AND CARBON TETRACHLORIDE.

Range of Pressure. kg./cm².	Chloroform. $(\beta-\beta')10^6$.	CCl_4 $(\beta-\beta')10^6$.	Compressibility of Chloroform $(\beta 10^6)$	Compressibility of Carbon Tetrachloride $(\beta 10^6)$.
0–100	[87.6]	[86.2]	[91.4]	[90.0]
100–200	82.7	82.8	86.4	86.6
200–300	73.5	78.2	77.2	82.0
300–400	66.5	70.5	70.2	74.2
400–500	61.7	65.0	65.3	68.6
500–600	57.5	61.1	61.1	64.7

As before, the curve below 100 atmospheres is partly extrapolated, hence the first figure is uncertain in each case. The values are very consistent and are not far different, for the two liquids, each being about one and a half times as compressible as bromine. It is remarkable and an interesting fact that although the carbon tetrachloride is at first slightly less compressible than chloroform, above 200 atmospheres, the relative magnitudes are reversed, since the compressibility of the former substance diminishes less rapidly than that of chloroform with increasing pressure. This point will be referred to again.

It is worthy of note that Grassi found the compressibility of chloroform to increase with increasing pressure below 10 atmospheres. Whether this is an inaccurate observation, or whether an anomalous behavior really occurs at low pressures, it is impossible to ascertain without further data. It is our intention to pursue the question. Since Grassi's values were obtained at 12° they are not directly comparable with ours. In any case, the present observations establish beyond doubt the fact that at high pressures chloroform decreases in compressibility with increasing pressure in the usual way.

From the great compressibility of these liquids, consisting chiefly of chlorine, and possessing boiling points not far from bromine, it seems certain that chlorine must be much more compressible than bromine under similar circumstances. In order to obtain further light upon this important question, which cannot be easily answered by direct ex-



Cl_2
CCl_4
$CHCl_3$
Br_2
$CHBr_3$
H_2O
P
3.0
2.5
2.0
1.5
1.0
PRESSURE
100
200
300
400
500

FIG. 5.

periment, we thought it worth while to determine the compressibility of bromoform, because of its close analogy to chloroform.

Bromoform.

Merck's "chemically pure" bromoform boiling between 150.3° and 150.5°[1] was used. Perkin[2] found the specific gravity of this substance to be 2.903 at 15°/15°, and 2.883 at 25°/25°. These values reduce to 2.900 at 15°/4° and 2.875 at 25°/4°, from which by interpolation we obtain the value 2.888 at 20°/4°.

The determination of the compressibility of bromoform was made in the special jacket (No. IV) devised for the determination of the compressibilities of liquids which do not attack mercury. It was found during the course of the experiment that a slight action between mercury and bromoform had nevertheless taken place; yet the results can hardly have been vitiated to an extent exceeding one per cent., and for the purpose of this part of the work, namely, the fixing of the position of the compressibility of chlorine with relation to those of the other halogens this degree of accuracy is all that is needed. The method of experimentation is evident from the following sketch and descriptions.

The jacket full of mercury weighed 291.6 grams, while the weight of the bromoform, partly replacing the mercury, was 54.63 grams.

Data for Bromoform.

Series.	Observed Pressure.	Total Hg Added.	Percentage Change in Volume of Bromoform Minus that of Mercury = $(\beta-\beta')P$.
14	32	0	0.145
	164.5	1.546	0.727
	360	3.591	1.494

From these data, plotted, the compressibility results for bromoform are readily found to be the following:

Compressibility of Bromoform.

Range of Pressure kg./cm².	$(\beta-\beta')10^6$.	$\beta.10^6$.
0–100	45.3	49.1
100–200	42.0	45.8
200–300	38.8	42.5
300–400	36 8	40.5

Thus the compressibility of bromoform is somewhat less than that of bromine, being about thirteen times as great as that of mercury. Bromoform is only about half as compressible as chloroform.

[1] Corrected for exposed column, under 760 mm. pressure.

[2] Journal Prakt. Chem. (2), 32, 523 (1885).

The Probable Compressibility of Chlorine.

It has already been suggested that there is good reason for believing that chlorine is much more compressible than bromine. There are indeed at least three reasons for this belief, namely: first, the fact that chloroform and carbon tetrachloride are both much more compressible than bromine, although their boiling points are no lower; secondly, because bromoform is so much less compressible than the analogous chloroform; and thirdly, because bromine is so much more compressible than iodine, a fact which leads one to infer that chlorine would be yet more so, because of the well known periodicity of these elements.

There are at least two ways in which a quantitative estimate may be formed of the compressibility of chlorine. Fortunately the differences between the boiling points of chloroform and bromoform (152° — 61° = 91°) is almost exactly the same as the difference between the boiling points of chlorine and bromine (60° — (— 32°) = 92°); or, to express the same relation in another way, the boiling point of chlorine is as much below that of chloroform as that of bromine is below that of bromoform.[1] Thus the effect of the internal pressure of cohesion, as indicated by the different boiling point, upon the compressibility in the former case may be assumed to be the same as the known effect in the latter case. Overlooking other minor differences, such as the absolute temperature and the possibly varying effect of the hydrogen and carbon (which however probably constitute only a small proportion of the volume of chloroform and bromoform), it may be supposed that the following equation holds approximately true:

$$\beta_{Cl} = \beta_{CHCl_3} \frac{\beta_{Br}}{\beta_{CH\,Br_3}}$$

From the figures already given for the variables in the right hand member of this equation, it is easy to compute the following values

[1] The boiling points of the halide substitution products of methane are interesting in their regularity. Each substitution of bromine for chlorine involves a rise of boiling point of about 28°. This regularity, which is shown in the table below, supports the method of approach used above.

Substance.	Boiling Point.	Substance.	Boiling Point.	Difference.	
Cl_2	−32°	Br_2	+60	92°	
CCl_4	+77	CBr_4	+[illegible]	112	= 4 × 28
$CHCl_3$	+61	$CHBr_3$	+152	91	= 3 × 30
CH_2Cl_2	+[illegible]	CH_2Br_2	+97	55	= 2 × 27
CH_3Cl	−[illegible]	CH_3Br	+5	27	= 27
CH_4	[illegible]	CH_4		0	

for the left hand member for each successive hundred units of pressure, namely: 114, 106, 96, 87, 81. Similar, though somewhat lower results are found if an *additive* instead of a *proportional* relation is assumed.

Another method of computing any property of chlorine is by extrapolating that property of bromine and iodine.

In some cases, such as the atomic weights and volumes, the relation is almost linear; in such cases extrapolation of this kind is moderately accurate in its results. Compressibility, being a volume function, may also be assumed to vary in approximately linear fashion. Upon this assumption, the compressibility of chlorine would be that of bromine plus the difference between that of bromine and iodine. The values thus obtained agree surprisingly well with those given above, as may be seen from the following table.

PROBABLE COMPRESSIBILITY OF CHLORINE AT 20° C.

Range of Pressure. Kg./cm^2.	Calculated from Chloroform and Bromoform. $\beta 10^{-6}=$	Calculated from Bromine and Iodine $\beta 10^{-6}=$	Average $\beta . 10^6$
0–100	114	109	112
100–200	106	109	107
200–300	96	101	98
300–400	87		87
400–500	81		81

This curve is plotted in a dotted line on the diagram (Fig. 5). It makes no pretensions to accuracy, but serves to give an approximate idea of the probable magnitude of the quantity in question. It will be seen that chlorine is probably nearly twice as compressible as bromine and thirty times as compressible as mercury.

PHOSPHORUS.

The material used was the purest commercial pale yellow phophorus, which was fused under water and cast into sticks of suitable size. These sticks were cut into lengths of about half a centimeter each, in order to disclose occasional cavities. All imperfect pieces were of course rejected. The specific gravity, according to the recent determinations of Pisati and de Francius,[1] is 1.823. The phosphorus was weighed under water after washing with alcohol and ether and drying.

Phosphorus attacks mercury too vehemently to be immersed directly in the mercury of the glass jacket. It was therefore packed into a thin glass tube containing water; and in order to be handled more

[1] Berichte d. deutsch ch. Ges. 8, 70 (1875).

readily, this tube was closed with a slightly lubricated stopper containing a single fine orifice. This tube thus filled was attached to a small hook on the inside of the glass jacket, a profitable precaution which prevented the inner tube from rising by its great buoyancy and cutting off the electrical connection, as well as facilitated the filling of the jacket with mercury.

After adding successive amounts of mercury to the jacket thus filled, applying the corresponding pressures, and thus determining the pressure-volume relations of this complex system, the phosphorus was removed, and its place was filled by precisely the same volume of mercury, everything else remaining unchanged. The compression experiments were then repeated, and the difference between the two series obviously gave at once the difference of compression between the given volume of phosphorus and mercury.

Two entirely independent sets of experiments were made, every detail of the operation being repeated. Their very satisfactory agreement not only shows that no trivial errors of recording were made, but also affords excellent evidence of the accuracy of the method. The values marked with asterisks were obtained by *removing* small amounts of mercury after the maxima had been reached. Their exact coincidence with the appropriate curves drawn through the other points showed that no permanent "set" had been caused by the application of the high pressures.

The results of the two complete sets are given below. The weight of the phosphorus in the first case was 8.304 grams, and in the second case 8.283 grams.

Upon plotting these values, regular curves are obtained which, when

DATA FOR COMPRESSIBILITY OF PHOSPHORUS 20° C. (COR.).

Series 15 with Phosphorus.			Series 16 with Mercury.		
Pressures (kg./cm².)	Weight of Hg Added.	Same + a_n = Ordinate of Curve.	Pressures (kg./cm².)	Weight of Hg Added.	Same + a_n = Ordinate of Curve.
62.5	0	[0.242 = a_{15}]	95	0	[0.265 = a_{16}]
197.5	0.510	0.753	217.5	0.337	0.602
338.5	1.018	1.260	350	0.679	0.944
482.5	1.525	1.767	477.5	0.995	1.260
*358.0	*1.089	1.331	*195.5	*0.261	0.526
*160.5	*0.376	0.618			
Series 17 with Phosphorus.			**Series 18 with Mercury.**		
53	0	[0.204 = a_{17}]	65.5	0	[0.183 = a_{18}]
199.5	0.551	0.755	176.5	0.306	0.489
337.5	1.051	1.255	310	0.661	0.844
480.0	1.552	1.756	432	0.973	1.156
*178	*0.474	0.678	*177	*0.306	0.489

superposed in the usual manner, give very consistent values. The averages are given below, together with the compressibility of phosphorus computed from them, for each 100 units of pressure. The quantity $A - B$ represents the value in the large brackets of equation (5), from which $\beta - \beta'$ is easily calculated.

COMPRESSIBILITY OF PHOSPHORUS.

Abscissæ Pressures. kg./cm².	Ordinates.		$A - B$.	$(\beta - \beta')10^6$ for Each Successive 100 Pressure Units.	$\beta \cdot 10^6$.
	A = Curve of P_4.	B = Curve of Hg.			
0	0	0	0		
100	0.385	0.280	0.105	17.1	20.9
200	0.759	0.552	0.207	16.6	20.4
300	1.124	0.817	0.307	16.2	19.9
400	1.480	1.074	0.406	16.1	19.8
500	1.829	1.325	0.504	15.9	19.6

Thus the compressibility of phosphorus is about half that of water and more than five times that of mercury.

WATER.

Four reasons make it desirable to determine the compressibility of water. In the first place, this liquid could be accurately used in both forms of apparatus, and hence could serve as a certain means of comparing the results of each. Again, so many investigators have determined this quantity that it serves as an excellent means of comparing our method with those of others. Further, the value obtained by our present apparatus may at some future time, by comparison with the results of an experimenter with a perfect pressure gauge, serve conveniently to determine by backward calculation the error of our pressure-gauge, and thus correct all the results in this paper. Finally, the compressibility of water at pressures above 262 atmospheres seems never to have been determined.

The water used in the determinations described below was purified by two successive distillations, the first one being from permanganate solution. It was boiled just before being used, to expel the air.

As has been stated, its compressibility was determined in two ways, first, by the method used with the bromine; and second, by the method first used with bromoform, namely by means of the jacket devised for liquids which do not attack mercury.

Three series are recorded below. No. 19 was made by the first method, and Nos. 20 and 21 by the second method. The corresponding glass jackets were II and IV, containing when full 437 and 291.6 grams of mercury respectively. The weights of water were 4.165 and

18.725 grams (corrected to vacuum) respectively. The weight of the thin bulb in series 19 was 1.09 grams — of course none was used in Series 20 and 21.

Series.	Observed Pressure.	Actual Weight of Mercury Added.	Volume Decrease in Water Minus Ditto in Mercury.
	kg./cm².	grams.	per cent.
19	43	0	$(0.179 = a_{19})$
	137	0.2778	0.569
	237	0.5600	0.960
	350	0.8516	1.356
20	20.5	0	$(0.084 = a_{20})$
	118	1.034	0.474
	216.5	2.045	0.855
	310.5	2.991	1.212
	406.5	3.911	1.559
21	35	0	$(0.144 = a_{21})$
	232	2.053	0.919
	331	3.041	1.292

These figures are plotted as usual on the diagram (Fig. 5), and yield a curve of the same type as the others, with very few discrepant points. The highest results of each series falls exactly upon the curve, showing that the methods give identical results within the necessary limits of error of each. Hence the thin glass bulb used in Series 19, as well as earlier in Series 1 to 13, introduced no appreciable error. It is worthy of note also that the compressibility of a saturated solution of iodine in water may be computed from the experiments on iodine, and is found thus to be less than one per cent. different from that of pure water at each point in the curve. The small magnitude of this difference confirms both the work and the calculation of the iodine results.

From the curve given on the diagram the compressibility of pure water may be found as follows:

Compressibility of Water.

Range of Pressure kg./cm².	$(\beta-\beta')\,10^6$.	$\beta\,10^6$.
0–100	[40.5]	[44.3]
100–200	39.5	43.3
200–300	37.3	41.0
300–400	36.6	40.3
400–500	35.0	38.6

Thus water is between eleven and twelve times as compressible as mercury, and about half as compressible as chloroform.

Other experimenters have rarely used 20° as their standard temperature, hence their results must be reduced before comparison with ours. Several investigators have shown that the compressibility of water

increases with decreasing temperature, a somewhat unique phenomenon. There is no doubt that the anomaly is connected with the anomalous temperature coefficients of other properties of water, and may be supposed to be due here also to the increasing presence of a more bulky polymer at lower temperatures. With the help of the table given on page 269 of the admirable book of Landolt and Börnstein (1894), it is easily possible to make an approximate correction for temperature. Corrected in this way to 20°, and also transposed from the "atmosphere" to the metric unit, some of the values found for the compressibility of water are given in the following table:

Thus our result accords closely with the higher value found by Tait and with the results of Pagliani and Vicentini, Avenarius, Grinaldi, Schneider, and Röntgen and Schumann. It is somewhat higher than the values found by Drecker and Amagat, and the second value found by Tait.

COMPRESSIBILITY OF WATER.

COMPARISON OF WORK BY DIFFERENT EXPERIMENTERS.

Range of Pressures.	Investigator.	$t°$	$\beta_{t°}\cdot 10^6$ Recip. Atmospheres.	$\beta_{20}\cdot 10^6$ Recip. kg./cm².
Low pressures.	Röntgen and Schneider.	18.0°	46.2	44.3
	Tait.	12.	48.0	44.6
	Tait.	10.	44.2	40.3
	Schumann.	17.1	45.9	43.9
	Drecker.	20.	43.8	42.4
	Average, Pagliani, Vicentini, Avenarius, Grinaldi.	20.	46.1	44.6
0–100	Richards and Stull.	20.	45.8	44.3
0–262	Amagat.	17.6	42.9	41.0
0–262	Richards and Stull.	20.	44.5	43.1

The close agreement of our value (44.3) with that accepted as the most probable [46.09 (1000/1033) = 44.6] by Landolt and Börnstein (1894, page 269), is very satisfactory, especially since the slight difference of less than one per cent. is probably due to the low pressures used in obtaining the higher of the two results.

The agreement is close enough to show that the measurement of pressure — the least certain part of our determination — must have been essentially correct. This conclusion affords valuable verification of the present measurements of all the other substances as well as of water.

THE HEAT OF COMPRESSION.

It has been already shown in the early part of this paper that the heating of the compressed material causes a thermal expansion so great as to cause the first breaking of the galvanic current in the jacket to

occur at a much higher pressure than the true pressure corresponding to isothermal compression. Since the substance itself is the measuring medium, it was thought possible that this instant self-heating effect might afford a means of avoiding the lag which any form of thermometer must involve, and thus give a truer measure of the adiabatic rise of temperature on compression than any method involving a thermometer.

In the case of mercury (in jacket IV), contact was at first broken upon rapid compression at 500 $kg./cm^2$. with a quantity of mercury which finally gave a reading of 366 $kg./cm^2$. when the heat of compression had been taken away. Thus the pressure of 500 atmospheres caused a rise of temperature enough to cause an error of 134 atmospheres, which corresponds to an increase in the volume of the mercury of 0.0040 milliliter, a value taken from the curve for this jacket or easily calculated from the mercury-glass curve given on page 19.[1]

There were present 21.6 milliliters of mercury, hence the percentage expansion was 0.0185. But a rise of 1° would cause an expansion of 0.0157 per cent. if the glass were warmed also to the same extent, or 0.0182 if the glass were stationary in temperature. Hence the rise of temperature on compressing the mercury to 500 atmospheres must have been somewhere between 1.2° and 1.0°, according to the supposition adopted concerning the glass. The higher of these two results is the more probable, and even this may be too low because of the exceedingly rapid loss of heat from this system assumed to be in an adiabatic condition.

Another mode of stating this calculation may make the matter clearer. The coefficients of cubic expansion and compressibility are respectively represented by the ratios $(\delta v/\delta t)_p$ and $(\delta v/\delta p)_t$. If now we make $(\delta v)_p = (\delta v)_t$ — a proceeding actually carried out in the above experiment — the following equation is obtained by dividing one by the other.

$$\frac{\delta t}{\delta p} = \frac{\text{coeff. of compress.}}{\text{coeff. of expans.}}.$$

From this equation

$$\delta t = \frac{134 \times 0.0000014}{0.000157} = 1.2,$$

a result identical with that obtained before. In this case, of course, since the actual change of pressure is the value used in the expression,

[1] The change of compressibility with temperature and pressure are neglected in this calculation as being infinitesimals of the second order.

the actual coefficients corresponding to the mercury and glass together must be used in the calculations.

The heat of compression of a cubic centimeter of mercury over the pressure range of 500 atmospheres is thus about $13.5 \times 1.2 \times 0.033 \times 4.2 = 2.3$ joules. This value is probably too low rather than too high.

In the case of water the pressure-difference between the adiabatic and isothermal readings was much smaller, being only 9.5 units of pressure for a pressure range of 416 units. Since in the experiment with this same jacket containing water, 97.5 units of pressure corresponded with 1.034 grams of added mercury, the difference of 9.5 units must have signified an addition of 0.10 gram or 0.0075 milliliter of mercury. The volume of water was 18.75 milliliters, hence the percentage expansion was 0.040. But a rise of temperature of 1° would cause a percentage expansion of about 0.02, hence the rise of temperature must have been about 2°. This signifies the evolution of nearly 9 joules of heat under compression to 416 units of pressure, or about 11 joules under compression to 500 units of pressure. The amount is large, being nearly five times as great as the corresponding heat of compression of mercury. In this case, as in the preceding one, the cooling effect probably introduces a large error; the results are given as preliminary examples of an application of the apparatus, rather than as a precise evaluation of the effect. With greater precautions a more exact result might be obtained; and we hope to test the method further.

A High Pressure Manometer and the Unit of Pressure.

The properties of a few pure substances serve as the most convenient and generally useful means of defining by comparison the properties of all substances and the various dimensions of energy. Thus specific gravities and specific heats usually serve as the means of determining densities and heat capacities; the temperature scale is defined by the triple or quadruple or other fixed points of a few elements or simple compounds and subdivided by the tension-increase of hydrogen in constant volume; electromotive force is found by comparison with a Clark or Weston cell; electrical quantity is determined by the weight of a pure metal which it can deionize, and so forth. It seems to us desirable to define the measurement of high pressures also in an equally convenient way by reference to the compressibility of one or more easily obtained pure liquid substances. The problem is a difficult one, because the apparatus used for containing the material may

be distorted by the strain of compression; but with the help of our glass jacket the result is very easily attained.

If glass were a definite substance, the figures given in the table of data concerning the compressibility of water alone or of mercury alone, would at once afford the desired intelligence. By plotting the results in the second and third column on page 38 for example, it is readily seen that in a glass jacket containing 18.75 milliliters of water and 1.9 milliliters of mercury at 20°, 100 kilograms per square centimeter would correspond to 1.050 grams of added mercury, 200 units of pressure would correspond to 2.086 grams of added mercury and so forth. The same proportion of change of volume to total volumes of water and mercury would exist in a jacket of any other size. Unfortunately, however, the compressibility of glass is not uniform enough in different samples to make such an inference more definite than within three tenths of one per cent.

On the other hand, the *difference between the compression of water and mercury*, as found by a jacket of this kind, is perfectly definite and free from all uncertainty connected with the glass. This difference is plotted as the curve for water, on the larger diagram (Fig. 5), and will serve at any time as a means of comparing any other gauge with that made by Schaeffer and Budenberg, thus enabling any one who has a less accurate gauge to correct its readings, or any one who has a more accurate guage to correct ours.

The best method of making this comparison would be to make successive series of experiments first with mercury and afterwards with water in a given glass jacket, in the way described above, and then to plot the results and compare the differences with ours. The curves are so nearly straight lines that they may be drawn with great accuracy by bending a thin ruler made of wood with an even grain, until all the points are covered.

From our preliminary experiments it seems probable that the sensitiveness of this manometer is very great. Under favorable conditions the method is able to detect $\frac{1}{20}$ atmosphere in 1,000 atmospheres or one part in 20,000.

It is our purpose to carry out the evaluation of this manometric method with much greater precision than has been heretofore possible, in an apparatus free from ground glass joints. The present results in this direction must be considered as merely preliminary, but even these may serve an end hitherto unattainable.

It is a matter of great regret that the scientific world has not agreed upon a less arbitrary unit of pressure than the "atmosphere." The diffi-

culty is now increased by the frequent technical use of this word to designate the pressure of a kilogram per square centimeter. The growing tendency toward the adoption of the c.g.s. system suggests the use of a consistent unit for this dimension also. Might not the pressure of a dyne per square centimeter be suitably called a *bar?* (Greek βαρος, pressure, weight.) This suggestion is made because the practical use of a unit is always much facilitated by a definite verbal designation. In this case, the pressure of a megadyne per square centimeter would be called a *megabar*, a name no more cumbrous than atmosphere, and far more definite. This unit, though unnamed, has long been advocated by Ostwald as a more scientific one than the present standard.[1] The megabar is 1,000/980.6 = 101.98 per cent. of a kilogram per square centimeter, or 101.98/1,033.2 = 98.703 per cent. of an atmosphere, or the pressure measured by 75.015 centimeters of mercury at 0° C., at sea level, and 45° of latitude. This pressure is more nearly the average atmospheric pressure at the laboratories of the world than the arbitrary atmosphere usually taken. A megabar, acting through the volume of a cubic centimeter or milliliter, performs a megerg of work, or one-tenth of a joule. For the convenience of possible users of the new results, all are tabulated below on the basis of each one of these three standards of pressure.

TABLE OF COMPRESSIBILITIES AT 20° C.

The values given below are multiplied by 10^6 in order to economize space. Brackets signify partial extrapolation.

Range of Pressure.	I_2	Br_2	Cl_2	CCl_4	$CHCl_3$	$CHBr_3$	H_2O	P_4	Hg
kgs. per cm².									
0–100	[13]	[61.3]	[112]	[90.0]	[91.4]	[49.1]	[44.3]	[20.9]	3.80
100–200	13	56.3	[107]	86.6	86.4	45.8	43.3	20.4	3.75
200–300	12	52.7	[98]	82.0	77.2	42.5	41.0	19.9	3.72
300–400	—	50.2	[87]	74.2	70.2	40.5	40.3	19.8	3.69
400–500	—	48.1	[81]	68.6	65.3	[39.5]	38.6	19.6	3.64
megabars.									
0–100	[13]	[62.5]	[114]	[91.8]	[93.2]	[50.1]	[45.2]	[21.3]	3.88
100–200	13	57.4	[108]	88.3	88.1	46.7	44.1	20.8	3.82
200–300	13	53.7	[100]	83.6	78.7	43.3	41.8	20.3	3.79
300–400		51.2	[89]	75.7	71.6	41.3	41.1	20.2	3.76
400–500		49.0	[83]	69.9	66.6	[40.3]	39.4	20.0	3.71
atmospheres.									
0–100	[14]	[63.4]	[116]	[93.1]	[94.5]	[50.8]	[45.8]	[21.6]	3.92
100–200	13	58.2	[110]	89.6	89.4	47.4	[44.8]	21.1	3.87
200–300	13	54.5	[102]	84.7	79.8	43.9	42.4	20.6	3.84
300–400	—	51.9	[90]	76.7	72.6	41.1	41.7	20.4	3.81
400–500	—	49.7	[84]	70.9	67.6	[40.8]	39.9	20.2	3.76

[1] Grundriss allgem. Chem., p. 54 (1899).

Change of Compressibility with Pressure.

A glance at the above table shows that all the substances studied, like all those examined by Barus, show a decrease in compressibility with increasing pressure. This decrease is by no means a simple function, however. Leaving out of consideration the cases of chlorine and iodine, which cannot claim accuracy enough for serious consideration in a discussion of this kind, the other substances show the following percentage decrease in their compressibilities between 100 and 500 atmospheres: $CHCl_3$ 29, CCl_4, 26; Br, 21; $CHBr_3$, 20.6; H_2O, 13; Hg, 4. This order is arranged according to the magnitude of the compressibility, and it exhibits a steady decrease; hence one may infer that, other things being equal, the greater the compressibility, the greater is its percentage decrease with increasing pressure. That other circumstances influence this relation is shown however by the fact that chloroform and carbon tetrachloride manifest different second differential quotients although their first differential quotients are exactly identical at 150 atmospheres. Moreover, bromoform and water have almost the same compressibility, and yet the change of this compressibility with the pressure is noticeably different. Such differences as this must be referred to the specific natures of the component elements, and the internal pressure relations within each substance.

When the theorizer goes further than such a comparison as this, and attempts to determine the mathematical expressions for these curves, he is met by a serious obstacle. The departure from the perfectly linear equation $x = ay$ is not sufficiently greater than the possible error of the gauge to make its somewhat subtle nature clearly manifest. One should point out also the probability that the parabolic equations proposed by Barus for the organic liquids studied by him are subject to an even greater experimental uncertainty; so that it is safe to say that no data now known to us afford a satisfactory basis for the determination of the law underlying the change of compressibility with pressure. It is our hope, by more accurate experiments made upon larger quantities of material and with a more perfect gauge, to proceed further in this direction.

In conclusion, it is a pleasure to express our great indebtedness to the Cyrus M. Warren Fund of Harvard University for assistance in the early part of this investigation, and to the Carnegie Institution of Washington for assistance in the latter part.

SUMMARY.

In this paper the following additions to the knowledge of compressibility are made:

1. The practical errors of many previously used methods have been demonstrated.

2. New methods have been suggested which are applicable to nearly all solids and liquids.

3. With the help of these methods, the compressibility of bromine, iodine, chloroform, bromoform, carbon tetrachloride, phosphorus, water and glass have been determined by reference to mercury, in most cases as far as 500 or 600 atmospheres. These are recorded on p. 43.

4. From some of these the compressibility of liquid chlorine has been inferred.

5. Approximate determinations of the heats of compression of water and mercury have been made.

6. A new manometer for calibrating high pressure gauges is proposed.

7. The word *megabar* is suggested as a convenient name for the pressure of a megadyne on a square centimeter, and the use of this absolute standard is urged.

8. The compressibilities of the substances named above have been compared with regard to their relative decrease with increasing pressure. It is pointed out that usually the greater the compressibility the greater is its decrease with increasing pressure.